

20 JAN 1939

# PATENT SPECIFICATION

Convention Date (Germany) : June 23, 1936.

Application Date (in United Kingdom) : June 22, 1937.

(Divided out of No. 497,487.)

Complete Specification Accepted : Dec. 22, 1938.

497,721

No. 15885/38.



## COMPLETE SPECIFICATION

### Manufacture of Aromatic Compounds Alkylated in the Nucleus

We, I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT, a Joint Stock Company organised according to the laws of Germany, of Frankfurt a/Main, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The known processes for the nuclear alkylation of aromatic compounds containing hydroxyl groups by means of olefines include condensation with the aid of boron trifluoride - see Specification No. 307,802.

The latter describes the condensation of cresol with ethylene in presence of boron trifluoride and gaseous hydrochloric acid at 200°C under 50 atmospheres pressure to give a mixture of alkylated cresol ethers and alkylated cresols. These known processes have proved unsatisfactory when applied to the nuclear alkylation of aromatic hydroxyl compounds by means of olefines containing 4 or more carbon atoms, since a considerable formation of alkyl ethers takes place and there are thus formed mixtures of products while the olefines are sometimes split into two or more olefines having a shorter chain.

U.S.A. Specification No. 2008032 describes a process of alkylating phenols by reacting them with ethylenic hydrocarbons in presence of a kationoid condensing agent. The method of working described involves the use of a solvent for one or both of the reactants; when sulphuric acid is used as the condensing agent this may also serve as the solvent. The use of boron trifluoride as a condensing agent is mentioned but specific directions concerning such use are lacking. Specification No. 431,487 contains somewhat equivalent disclosures in regard to the condensation of polyhydric phenols with di-isobutylene.

According to the present invention, alkyl groups having at least 4 carbon atoms may be advantageously introduced into aromatic compounds containing hydroxyl by means of olefines containing 4 or more carbon atoms in the molecule, without destruction of the olefine, by causing the olefine to act upon the liquid or molten aromatic hydroxyl compound in the presence of boron trifluoride in solu-

[Price 1/-]

tion in the liquid reaction mixture at temperatures below 100°C and at normal atmospheric pressure.

The products are aromatic hydroxyl compounds alkylated in the nucleus.

Among aromatic hydroxyl compounds suitable as parent materials for the invention may be named, phenol and cresols.

The boron trifluoride may be introduced into the aromatic hydroxyl compound, which is a liquid or is in the molten state, and the olefine added to, or led into this mixture, containing the boron trifluoride in solution, the temperature of the mixture being maintained below 100°C.

Alternatively the olefine in question is mixed with the aromatic hydroxyl compound and boron trifluoride is introduced into the mixture. The condensation completed, the boron trifluoride present in the mixture is washed out by means of water and the alkylated aromatic hydroxyl compound formed is freed from water by heating it, if desired under reduced pressure.

Some of the products obtained, especially when individual olefines are used, are crystalline bodies; when mixtures of olefines are used, there are generally formed oily to wax-like bodies. In most cases the alkylated aromatic hydroxyl compound may be formed in the presence of 1 per cent of boron trifluoride, calculated upon the amount of aromatic hydroxyl compound used. However, it is sometimes necessary to vary the proportion of boron trifluoride to suit the compounds that are to react, in order to obtain an almost exclusively nuclear alkylation. By increasing the proportion of olefine to aromatic hydroxyl compound used it is easily possible to introduce more than one alkyl radical into the aromatic compound. The yields of alkylated aromatic hydroxyl compounds are very good. They sometimes amount to 98 per cent. of the theoretical yields.

The following Examples illustrate the invention; the parts are by weight:

1. 940 parts of phenol are heated to 50°C and 9.4 parts of boron trifluoride are introduced at the same temperature. 1120 parts of di-isobutylene are added drop by drop at a temperature between 25°C and 30°C. After a further stirring

for two hours at 40°C, the whole is washed with water. The dried product solidifies to a crystalline mass and proves to be nearly pure iso-octylphenol. The yield amounts to 98 per cent. of the theoretical.

2. 940 parts of phenol are heated to 50°C and 94 parts of boron trifluoride are added thereto. 2240 parts of di-isobutylene are then added at 35°C and the di-isooctylphenol formed is worked up as indicated in Example 1. The yield amounts to 95 per cent of the theoretical.

3. 11 parts of boron trifluoride are introduced into 108 parts of ortho-cresol heated to 50°C. 112 parts of di-isobutylene are added drop by drop, at 30°C and the whole is worked up in the manner indicated in Example 1. By distillation under a pressure of 5 mm., an oil is obtained which distils at 140°C-148°C and solidifies on standing to a crystalline mass.

4. 94 parts of boron trifluoride are introduced into 940 parts of phenol heated to 50°C. At 25°C-30°C 1120 parts of di-isobutylene are added drop by drop, and 560 parts of isobutylene are then caused to act, at a temperature of 30°C to 35°C, upon the iso-octylphenol thus obtained. The isobutyl-isooctylphenol thus formed is worked up as described in Example 1.

5. 10 parts of boron trifluoride are introduced, at 50°C into 94 parts of phenol. 56 parts of isobutylene are then introduced at 40°C-50°C. The para-tert-butylphenol thus produced solidifies to a crystalline mass and is washed with water

and filtered with suction. When using only 1 per cent. of boron fluoride, calculated upon the amount of phenol used, a product is obtained about a third of which consists of butyl-phenol ether.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A manufacture of aromatic hydroxyl compounds alkylated in the nucleus, by causing an olefine containing at least 4 carbon atoms to react with a liquid or molten aromatic hydroxyl compound in the presence of boron trifluoride in solution in the liquid reaction mixture at a temperature below 100°C and at normal atmospheric pressure.

2. A manufacture of aromatic hydroxyl compounds alkylated in the nucleus substantially as described with reference to any one of the Examples herein.

3. Aromatic hydroxyl compounds alkylated in the nucleus when prepared or produced by the process of manufacture particularly described and ascertained herein, or by any process which is an obvious chemical equivalent thereof.

Dated this 27th day of May, 1938.

ABEL & IMRAY,  
Agents for the Applicants,  
30, Southampton Buildings.  
London, W.C.2.

<p>85-039829/07 ATO CHIMIE</p> <p>28.06.83-FR-010631 (04.01.85) C08f-08 C08f-110/10 C09d-03/73</p> <p>Alpha, omega difunctional oligo-isobutylene prepn. - by soln. polymerisation of isobutylene in presence of boron tri-chloride, proton acceptor and diol, heating and fixing functional gps.</p>	<p>A17 X12</p> <p>AGOR 28.06.83 *FR 2548-194-A</p>	<p>A(2-A4, 2-B, 4-G5, 10-B8, 10-E1)</p> <p>240</p>
<p>C85-017173</p> <p><math>\alpha</math>-omega difunctional oligoisobutylenes are produced by:-</p> <p>(i) polymerising isobutylene at low temp. (pref. -70 to -20°C) in a solvent (pref. CH<sub>2</sub>Cl<sub>2</sub>) in the absence of moisture and in the presence of BCl<sub>3</sub>, a proton captor and a bissecondary or bitertiary, aromatic or aliphatic diol which can form carbocations under the action of BCl<sub>3</sub>;</p> <p>(ii) washing and isolating the obtd. oligoisobutylenes (I);</p> <p>(iii) converting (I) into <math>\alpha</math>-omega diunsaturated oligo-isobutylenes (II) by heating (pref. under vacuum at 100-150°C) and</p> <p>(iv) fixing functional gps. on (II) by a suitable reaction.</p> <p>Also claimed are (II) of mol. wt. 500-20000.</p> <p><u>USE/ADVANTAGE</u></p> <p>The prods. can react with other cpds. to give macro-mers and find applications in e.g. the prepn. of varnishes</p>	<p>and paints, special coatings, sealants or insulators for electrical equipment.</p> <p><u>PREFERRED MATERIALS</u></p> <p>The diol is 2,5-dihydroxy-2,5-dimethyl hexane; bis p-(2-hydroxy 2-propyl)benzene or 1,6-dihydroxy 1,6-diphenyl hexane.</p> <p>The proton captor is di-tert-butyl 2,6-pyridine (III).</p> <p><u>PREFERRED RATIOS</u></p> <p>Molar ratio isobutylene/diol is 10-50; BCl<sub>3</sub>/diol is 2-5; diol/proton captor is 5-10.</p> <p><u>FUNCTIONAL GP FIXATION</u></p> <p>Phenol gps. are fixed in <math>\alpha,\omega</math>-position or (II) by alkylation in presence of SnCl<sub>4</sub> at room temp. and carboxylic gps. are fixed by formylation in sulphuric medium.</p> <p><u>EXAMPLE</u></p> <p>(I) Synthesis of <math>\alpha,\omega</math>-dichloro-oligoisobutenes:-</p> <p>3.9 moles CH<sub>2</sub>Cl<sub>2</sub>, 4.5 x 10<sup>-3</sup> mole (III) and 1 x 10<sup>-2</sup> mole 2,5-dihydroxy 2,5-dimethyl hexane are placed in a reactor and cooled to -30°C and then degassed.</p>	<p>FR2548194-A*</p>

3.3 x 10<sup>-1</sup> mole isobutylene are added and reaction started by adding 3.4 x 10<sup>-2</sup> mole BCl<sub>3</sub>. After 2 hrs., the reaction is stopped with MeOH and the CH<sub>2</sub>Cl<sub>2</sub> removed.

(2) Conversion into α,ω-diunsaturated-oligoisobutenes:- The dichloro α,ω-oligoisobutene obtd. in (1) is heated under vacuum for 2-3 hrs. at 100-150°C. The by-prods. are removed by pumping under vacuum.

(3) Conversion into oligoisobutene α,ω-diphenol:- 2g of the prod. from (2), 0.7g phenol (molar ratio unsat./OH = 1/3) and 100 ml CH<sub>2</sub>Cl<sub>2</sub> are placed in a reactor and cooled to -30°C, followed by addition of 0.3 ml SnCl<sub>4</sub>. Reaction is effected for 1 hr. and stopped by adding MeOH. CH<sub>2</sub>Cl<sub>2</sub> is removed.

The desired prod. is obtd. by heating under vacuum at 100°C to remove the last traces of phenol. (8pp950BL DwgNo0/0).

FR2548194-A